Valence band photoemission from pure and Sr diffused single crystal anatase TiO_2(001) surfaces

S. Thevuthasan[1], V. Shutthanandan[1], M.A. Henderson[1], G.S. Herman[1,3], S.A. Chambers[1], C.H.F. Peden[1], S. Mun[2], N.M. Hamdan[2], D.K. Shuh[2], and C.S. Fadley[2]
[1]Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory
Richland, WA 99352, U.S.A.
[2]Lawrence Berkeley National Laboratory, Berkeley, CA 94720, U.S.A.
[3] present address: Hewlett-Packard Company, Corvallis, OR 97330, U.S.A.

INTRODUCTION

Titanium oxide is one of the most extensively studied transition metal oxides because of its availability and its wide use in a variety of technological applications. A large number of electronic, geometric , and catalytic studies of commercially available high-quality single crystal titanium oxide surfaces have been reported in the literature [1-3]. In contrast, although the anatase polymorph of titanium oxide show s a number of interesting chemical behaviors, including superior photocatalytic activities in comparison to rutile titanium oxide [4-7], investigations of high-quality anatase titanium dioxide are limited in the literature due primarily to the lack of availability of well-ordered single crystals.

Recently, single crystal anatase TiO_2(001) thin films were successfully grown on (001) surfaces of $SrTiO_3$ and $LaAlO_3$ surfaces using molecular beam epitaxy [8-10]. Surface structural study of these high quality single crystal films using angle-resolved mass spectroscopy of recoiled ions (AR-MSRI) [8] has identified a two domain (1x4) reconstruction on the anatase TiO_2(001) surface. It was suggested that the anatase (001) surface reconstructs to form a microfaceted surface that exposes (103) and (-103) surface planes. A missing oxygen row model was proposed from a low energy electron diffraction study, where the authors suggested a reduced surface was likely [9]. A subsequent scanning tunneling microscopy (STM) study confirmed the existence of the two domain (1x4) surface reconstruction of anatase (001) surface [10]. However, the authors described this reconstruction in terms of added and missing rows at the surface, which is slightly different from the previous two studies. A recent theoretical study by first principle density functional calculations proposed a fourth model, which is based on the replacement of bridging oxygen rows with rows of TiO_3 units and thus does not contain any reduced Ti^{3+} cation [11], consistent with x-ray photoemission (XPS) data [12]. In two of the experimental studies, core level x-ray photoelectron spectroscopy was used to investigate the electronic structure in the surface region and the authors did not observe any state due to reduced Ti^{3+} cation. Since core level XPS using conventional Al and Mg x-ray sources is sensitive to many layers in the surface region, it is difficult to obtain chemical properties of only the top most surface layer. Conventionally, valence band photoemission has been extensively used to address the issues related to the surface layer including the existence of surface states.

In a recent valence band investigation of single crystal anatase TiO_2 (101) surfaces using Al Kα x-rays, it was reported that the VB of anatase shows characteristics similar to those reported for the rutile polymorph [13]. In addition, no indications of intrinsic surface states were observed in this study. Although no intrinsic surface states were reported for clean un-reconstructed (101) surfaces, intrinsic surface states may exist for the (001) surface because of its two domain (1x4) reconstruction. In order to investigate this, we have carried out a series of valence band photoemission measurements at the Advanced Light Source (ALS) using high quality single

crystal anatase TiO_2(001) films grown on $SrTiO_3$(001) substrates. We also investigated the effects of Sr diffusion in the VB photoemission from these samples.

EXPERIMENT

The growth of anatase TiO_2(001) were carried out in an oxygen plasma assisted molecular beam epitaxial system (OPA MBE) described elsewhere [14]. Pure single crystal 1cmx1cmx1mm $SrTiO_3$(001) substrates were used in this study. Two clean Ta clips were used to hold the sample on the sample holder and a pair of thermocouples were fastened to the sample holder under one clip near a corner of the sample for temperature measurements. Before each growth, the substrates were cleaned using the oxygen plasma at a sample temperature of 950 K at P_{O2} = $2.0x10^{-5}$ Torr. The growth temperature was maintained at 875 K to avoid Sr diffusion into the film at high temperatures. During the growth, the Ti flux was evaporated from an e-gun emitter source in the presence of the oxygen plasma. In addition, oxygen pressure in the chamber was maintained at $1.5x10^{-5}$ Torr. In-situ XPS and ex-situ Rutherford backscattering spectrometry (RBS) along with x-ray diffraction was used to characterize these films. After these characterizations at the Environmental Molecular Sciences Laboratory, the samples were brought to the Advanced Light Source (ALS) for the valence band photoemission measurements at beam line 9.3.2. The end station at this beam line is equipped with Scienta SES 100 hemispherical analyzer for collection of photoelectron spectra, along with a five-axis sample manipulator and in-situ sample cleaning capabilities. The samples were cleaned and ordered by cycles of light 500 eV Ar^+ ion sputtering, annealing in oxygen at a pressure of $1x10^{-6}$ Torr and a temperature of 800 K.

RESULTS

Fig. 1 shows the valence band (VB) spectrum from a clean (1x4) reconstructed anatse TiO_2(001) surface. A photon energy of 80 eV was used to collect the photoelectrons at normal emission. This spectrum is similar to the spectrum reported for anatase TiO_2(101) [13] and it shows a wide O 2p feature, which is similar to the O 2p feature from the rutile TiO2 [15-17], centered around

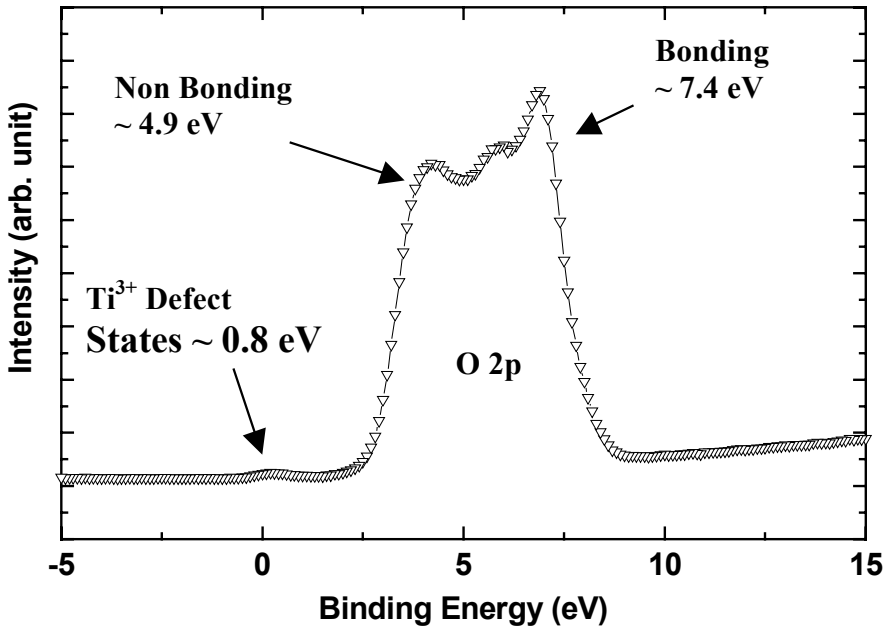

Fig. 1: Valence band spectrum from clean (1x4) anatase TiO_2(001) surface

6.5 eV. The width of this feature is about 4.7 eV and it consists of photoelectron contribution from π bonding (non bonding, peak at ~ 4.9 eV) and σ bonding (bonding, peak at ~ 7.4 eV) O 2p-Ti 3d orbitals. The band gap is about 3.1 eV and the feature at about 0.8 eV from the Fermi level is due to Ti^{3+} defect states related to the remnant of sputtered defects, which were not completely healed during the annealing in oxygen. No surface state associated with two domain (1x4) surface reconstruction was visible in the spectrum.

During the experiments, several mild sputtering and vacuum and oxygen annealing cycles were carried out to enhance Sr diffusion to the surface of the film. At the end of these processing cycles, about 1-2% of Sr was accumulated at the surface. These surfaces still showed a (1x4) surface reconstruction and VB spectra were collected from Sr diffused surfaces at normal and glancing emission. No differences between these spectra and the VB spectra from the clean surface were observed. The absence of any change in the VB spectra within our experimental uncertainties suggests that the Sr diffusion in small amounts did not alter the electronic structure of the anatase (001) surface.

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Principal investigator: S. Thevuthasan, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory. Telephone: 509-376-1375. Email: theva@pnl.gov.